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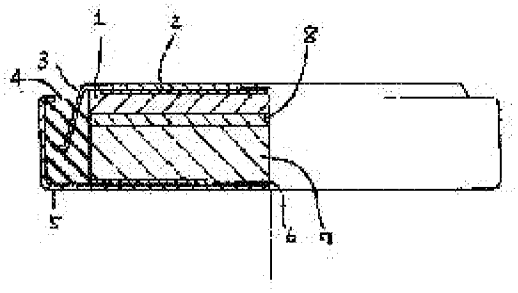
(54) **NON-AQUEOUS ELECTROLYTE BATTERY**

(57)Abstract:

PROBLEM TO BE SOLVED: To enhance the preserving characteristics of a non-aqueous electrolyte battery which uses lithium as a negative electrode active material by adding a specific quantity of 2-picoline or the like to non-aqueous electrolytic solution.

SOLUTION: A non-aqueous electrolyte battery is composed of a positive electrode, a negative electrode using lithium as active material, and a non- aqueous electrolytic solution, wherein at least one of the 2-picoline, 3-picoline, 4-picoline, 2,4-dimethylpyridine, piperazine, pyridazine, pyrimidine, pyrazine, 1,3,5-triazine, and 1,2,4,5-tetrazine is added in an amount of 0.01-20.0wt.% of the electrolyte. When the battery is in storage, its self-discharging is inhibited so that the preserving characteristics are enhanced.



DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention]This invention relates to improvement of the conservation characteristic of the nonaqueous electrolyte battery which used lithium as negative electrode active material, i.e., a lithium cell.
[0002]
[Description of the Prior Art]The lithium cell using lithium as negative electrode active material attracts attention as a high energy density battery.
Active research is done.

[0003]As a solvent which generally constitutes a nonaqueous electolyte from this seed cell, ethylene carbonate, Independence, such as propylene carbonate, butylene carbonate, dimethyl carbonate, diethyl carbonate, sulfolane, 1,2-dimethoxyethane, a tetrahydrofuran, and 1,3-dioxolane, two ingredients, or a ternary mixture is used. As a solute dissolved into this, and $LiPF_6$, $LiBF_4$, $LiClO_4$, $LiCF_3SO_3$, LiA_SF_6, $LiN(CF_3SO_2)_2$, $LiCF_3(CF_2)_3SO_3$, etc. can be enumerated.

[0004]By the way, such an independent solvent, two ingredients or a three-ingredient mixed solvent, and the nonaqueous electolyte that consists of solutes have a problem to which the cell capacity after preservation falls in order to cause a reaction with a chemical negative electrode which uses a solvent and lithium as an active material. Therefore, it has been important SUBJECT in utilization of this seed cell to control the self-discharge at the time of preservation. For example, as indicated by JP,49-108525,A, an electrolysis solution has the method of adding pyridine in order to raise a conservation characteristic, but still sufficient characteristic is not obtained in this method, but there is room of improvement.
[0005]
[Problem(s) to be Solved by the Invention]This invention controls the self-discharge at the time of saving this seed cell, and proposes the outstanding nonaqueous electolyte which raises a conservation characteristic.
[0006]
[Means for Solving the Problem]This invention is the nonaqueous electrolyte battery provided with an anode, a negative electrode which uses lithium as an active material, and a nonaqueous electolyte, 2-picoline, 3-picoline, 4-picoline, 2, 4-lutidine, A piperazine, pyridazine, pyrimidine, pyrazine, 1,3,5-triazine, At least one sort

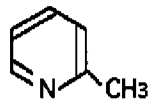
of additive agents chosen from a group which consists of 1, 2, 4, and 5-tetrazine are characterized by being added by said nonaqueous electolyte in 0.01 to 20.0% of the weight of the range to weight of said nonaqueous electolyte, and the addition effect is checked in this range.

[0007]Here, a structural formula of 2-picoline is shown in ** 1.

[0008]

[Formula 1]

2-ピコリン

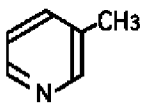


[0009]The structural formula of 3-picoline is shown in ** 2.

[0010]

[Formula 2]

3-ピコリン

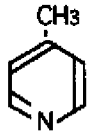


[0011]A structural formula of 4-picoline is shown in ** 3.

[0012]

[Formula 3]

4-ピコリン

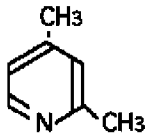


[0013]The structural formula of 2 and 4-lutidine is shown in ** 4.

[0014]

[Formula 4]

2,4-ジメチルピリジン

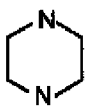


[0015]The structural formula of a piperazine is shown in ** 5.

[0016]

[Formula 5]

ピペラジン

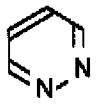


[0017]The structural formula of pyridazine is shown in ** 6.

[0018]

[Formula 6]

ピリダジン



[0019]The structural formula of pyrimidine is shown in ** 7.

[0020]

[Formula 7]

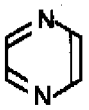
ピリミジン

[0021]The structural formula of pyrazine is shown in ** 8.

[0022]

[Formula 8]

ピラジン

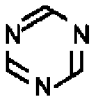


[0023]The structural formula of 1,3,5-triazine is shown in ** 9.

[0024]

[Formula 9]

1,3,5-トリアジン

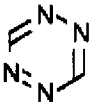


[0025]The structural formula of 1, 2, 4, and 5-tetrazine is shown in ** 10.

[0026]

[Formula 10]

1,2,4,5-テトラジン



[0027]Also in said additive agent, one sort in 2-picoline, pyrazine, and 1,3,5-triazine is considered to form the tunic optimal on a negative electrode, and is especially preferred. It is presumed that this is because the electron distribution of each structure has a gestalt which reacts to a lithium metal easily or it is because the

structure expressed with ** 1, ** 8, and ** 9 has the structure of being easy to approach lithium and being easy to react. As a result, in these, control of the rate of self-discharge is much more attained.

[0028]And it is much more preferred to consider it as 0.01 to 10.0% of the weight of the range to the weight of said nonaqueous electolyte as an addition of said additive agent, and it is preferred from a viewpoint of controlling the fall of the service capacity after preservation of this seed nonaqueous electrolyte battery.

[0029]As a solute of this seed cell, $LiPF_6$, $LiBF_4$, Although $LiClO_4$, $LiCF_3SO_3$, LiA_SF_6, $LiN(CF_3SO_2)_2$, $LiCF_3(CF_2)_3SO_3$, etc. can be used, it is not limited to this.

[0030]As a solvent of this seed cell, ethylene carbonate, propylene carbonate, butylene carbonate, dimethyl carbonate, diethyl carbonate, sulfolane, 1,2-dimethoxyethane, a tetrahydrofuran, 1,3-dioxolane, etc. can be used.

[0031]Although a metallic oxide containing manganese, cobalt, nickel, vanadium, and at least one sort of niobium can be used as an anode of this seed cell, it is not limited to this.

[0032]As a negative electrode of this seed cell, what uses a lithium ion as occlusion and a substance which can be emitted, and uses metal lithium as an electrode material electrochemically is illustrated. Electrochemically a lithium ion as occlusion and a substance which can be emitted, Lithium alloys, such as carbon materials, such as black lead, corks, and an organic matter baking body, and a lithium aluminum alloy, a lithium Magnesium alloy, a lithium indium alloy, a lithium tin alloy, a lithium thallium alloy, a lithium lead alloy, and a lithium bismuth alloy, are illustrated.

[0033]Black lead is the most preferred also in a carbon material at a point that especially a carbon material is preferred and high capacity at a point which does not have fear of an internal short circuit resulting from growth of electrocrystallization lithium of arborescence in this.

[0034]By the way, 2-picoline as an additive agent, 3-picoline, 4-picoline, If a specific amount **** nonaqueous electolyte is used, this additive agent will react one sort in 2,4-lutidine, a piperazine, pyridazine, pyrimidine, pyrazine, 1,3,5-triazine, and 1,2,4,5-tetrazine to lithium, and a good tunic is formed on a negative electrode. Since this tunic controls direct contact of lithium and a solvent, it controls disassembly of a nonaqueous electolyte which makes contact with lithium and an electrolysis solution **. Thus, it becomes possible to raise the conservation characteristic of a cell.

[0035]

[Embodiment of the Invention]Below, it explains in full detail per example of this invention.

(Experiment 1) The half section figure of the flat form nonaqueous electrolyte battery as one example of this invention is shown in drawing 1. The negative electrode 1 which consists of lithium metals is stuck to the inner surface of the negative pole collector 2 by pressure, and this negative pole collector 2 has adhered to the inner bottom of the negative electrode can 3 of a sectional view U shape which consists of ferritic stainless steel (SUS430). The peripheral edge of the above-mentioned negative electrode can 3 is being fixed to the inside of the insulating packing 4 made from polypropylene, it becomes a periphery of the insulating packing 4 from stainless steel, and the positive electrode can 5 which makes a sectional view U shape to a counter direction is being fixed in the above-mentioned negative electrode can 3. The positive pole collector 6 is being fixed to the inner bottom of this positive electrode can 5, and the anode 7 is being fixed to the inner surface of this positive

pole collector 6. Between this anode 7 and said negative electrode 1, the separator 8 with which the nonaqueous electolyte which is the main point of this invention was impregnated is infixed.
[0036]By the way, manganese dioxide heat-treated at the temperature of 400 ** is used for said anode 7 as an active material. Said heat treatment can be changed in a 350-430 ** temperature requirement. This manganese dioxide, the carbon powder as a conducting agent, and the fluororesin powder as a binder are mixed by the weight ratio of 85:10:5, respectively. Next, after carrying out pressing of this mixture, the drying process was carried out at 300 **, and the anode 7 was produced. It can set up and this drying process can be changed in a 250-350 ** temperature requirement.
[0037]On the other hand, said negative electrode 1 is produced by piercing a lithium rolled plate to a prescribed dimension.
[0038]As an electrolysis solution to and the thing which dissolved lithium trifluoromethanesulfonate in the mixed solvent (it is 5:5 at a volume ratio) of propylene carbonate (PC) and 1,2-dimethoxyethane (DME) at a rate of 1 mol/l. as a solute. 2-picoline as an additive agent is added at 0.5% of the weight of a rate, and a nonaqueous electolyte is obtained. this invention cell (the outer diameter of 20.0 mm and 2.5 mm in thickness) A was produced using this nonaqueous electolyte.
(Example 2) It replaced with 2-picoline used in said Example 1, and this invention cell B was similarly produced except having used 3-picoline as an additive agent.
(Example 3) It replaced with 2-picoline used in said Example 1, and this invention cell C was similarly produced except having used 4-picoline as an additive agent.
(Example 4) It replaced with 2-picoline used in said Example 1, and this invention cell D was similarly produced except having used 2 and 4-lutidine as an additive agent.
(Example 5) It replaced with 2-picoline used in said Example 1, and this invention cell E was similarly produced except having used the piperazine as an additive agent.
(Example 6) It replaced with 2-picoline used in said Example 1, and this invention cell F was similarly produced except having used pyridazine as an additive agent.
(Example 7) It replaced with 2-picoline used in said Example 1, and this invention cell G was similarly produced except having used pyrimidine as an additive agent.
(Example 8) It replaced with 2-picoline used in said Example 1, and this invention cell H was similarly produced except having used pyrazine as an additive agent.
(Example 9) It replaced with 2-picoline used in said Example 1, and this invention cell I was similarly produced except having used 1,3,5-triazine as an additive agent.
(Example 10) It replaced with 2-picoline used in said Example 1, and this invention cell J was similarly produced except having used 1, 2, 4, and 5-tetrazine as an additive agent.
(Comparative example 1) The same cell was produced using the electrolysis solution which does not add 2-picoline etc. as a comparative example, and this was made into the comparison cell X.
(Comparative example 2) It replaced with 2-picoline in said Example 1, the same cell was produced using the electrolysis solution which added pyridine, and this was made into the comparison cell Y. This cell is close to the technical thought indicated by JP,49-108525,B.
[0039]The conservation characteristic of each cell was compared using these this invention cell A-J and the

comparison cells X and Y. After this experimental condition produced each cell and saved it for two months at 80 **, it made the cell actually discharge and defined the rate of self-discharge (%) as a percentage to the capacity before saving that difference as compared with the capacity before preservation. This result is shown in Table 1.

[0040]

[Table 1]

	添 加 剤	自己放電率（%）
比較電池 X	な し	6．5
本発明電池 A	2－ピコリン	2．8
本発明電池 B	3－ピコリン	3．3
本発明電池 C	4－ピコリン	3．9
本発明電池 D	2,4-ジメチルピリジン	5．0
本発明電池 E	ピペラジン	3．2
本発明電池 F	ピリダジン	3．3
本発明電池 G	ピリミジン	3．1
本発明電池 H	ピラジン	2．4
本発明電池 I	1,3,5-トリアジン	2．6
本発明電池 J	1,2,4,5-テトラジン	3．0
比較電池 Y	ピリジン	5．8

[0041]In this table 1, this invention cell A-J shows that the rate of self-discharge is small, the fall of the cell capacity at the time of preservation is suppressed, and self-discharge is controlled as compared with the comparison cells X and Y.

[0042]this invention cell I which uses this invention cell H which uses this invention cell A which uses 2-picoline, and pyrazine as an additive agent, and 1,3,5-triazine. Also in this invention cell, the rates of self-discharge are 2.8%, 2.4%, and 2.6%, and are very small respectively, and it is **. He can understand having a **** conservation characteristic.

(Experiment 2) this invention cell A of said Example 1 and the cell which has the same composition were produced, the addition of 2-picoline added to a nonaqueous electolyte was changed, and the service capacity of the cell after preservation was measured. This experimental condition was saved for two months at 80 ** after producing each cell, and surveyed service capacity (mAh) of the cell.

[0043]This result is shown in Table 2. Table 2 shows the addition of 2-picoline and the relation of the rate of self-discharge (%) to nonaqueous electolyte weight. Calculation of this rate of self-discharge is the same as said experiment 1.

[0044]

[Table 2]

電池名	2-ピコリン添加量 (重量%)	自己放電率 (%)
比較電池	0	6．5
比較電池	0．001	6．5
比較電池	0．005	6．3
本発明電池	0．01	5．5
本発明電池	0．05	4．9
本発明電池	0．1	3．5
本発明電池	0．5	2．8
本発明電池	1．0	4．0
本発明電池	5．0	5．2
本発明電池	10．0	5．4
本発明電池	20．0	5．7
比較電池	30．0	9．0

[0045]As an addition of 2-picoline, to the weight of nonaqueous electrolyte, the addition effect was accepted in 0.01 to 20.0% of the weight of the range, and the fall of the cell capacity after preservation is controlled from this result. As this addition, the range of 0.01 to 10.0% of the weight of an addition is preferred from a viewpoint of not reducing service capacity of the cell after preservation.

[0046]As an addition, in 0.05 to 5.0% of the weight of the range, the rate of self-discharge will be 5.2% or less, and is the optimal.

[0047]Although the addition of 2-picoline is changed in the experiment 2, The same tendency is observed even if it is a cell using other additives, i.e., 3-picoline, 4-picoline, 2,4-lutidine, a piperazine, pyridazine, pyrimidine, pyrazine, 1,3,5-triazine, 1, 2 and 4, and 5-tetrazine.

[0048]Although lithium trifluoromethanesulfonate $LiCF_3SO_3$ was shown in each above-mentioned example as a solute dissolved in a nonaqueous electolyte, It cannot be overemphasized that $LiPF_6$, $LiClO_4$, $LiBF_4$, $LiN(CF_3SO_2)_2$, and $LiAsF_6$ can be used. Although the mixed solvent of propylene carbonate and 1 and 2-dimethoxyethane was illustrated as an organic solvent, It is possible to use these independence, butylene carbonate, ethylene carbonate, vinylene carbonate, dimethyl carbonate, diethyl carbonate, ethyl methyl carbonate, a tetrahydrofuran, 1,3-dioxolanes, and these mixtures.

[0049]

[Effect of the Invention]2-picoline, 3-picoline which are additive agents at a nonaqueous electolyte as mentioned above, The conservation characteristic of this seed cell can be raised by carrying out specific amount addition of the one sort in 4-picoline, 2,4-lutidine, a piperazine, pyridazine, pyrimidine, pyrazine, 1,3,5-triazine, 1, 2 and 4, and 5-tetrazine. And especially especially as said additive agent, one sort in 2-picoline, pyrazine, and 1,3,5-triazine is suitable. If an additive agent is added in 0.01 to 10.0% of the weight of the range to the weight of said nonaqueous electolyte also in a specific addition, the conservation characteristic of a cell

can be improved notably and the industrial value is very large.

[Translation done.]